Spin-reorientation process induced by an external magnetic field in erbium orthoferrite in the temperature range for ordering of the rare-earth ions

V. A. Klochan, N. M. Kovtun, G. A. Troitskiĭ, and V. M. Khmara

Donetsk Physico-technical Institute, Academy of Sciences, Ukrainian SSR
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Spin-reorientation processes that develop at helium temperatures in weakly ferromagnetic $ErFeO_3$ crystals, upon change of an external magnetic field applied along the crystallographic c axis, are studied experimentally, by the NMR method, and also theoretically. It is established that at temperatures above the critical temperature which is about 2.8 K, the processes occur continuously, as second-order phase transitions; but at temperatures below the critical, the transitions between phases are of the first order, and there appear two-phase states of the same type as the intermediate state in antiferromagnets. A phase diagram is plotted for the magnetic material, and on it the region of intermediate states is distinguished.

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In previous investigations of the magnetic structure of erbium orthoferrite, $ErFeO_3$, by the neutron-diffraction method[1,2] and by the NMR method,[3-5] it was observed that at helium temperatures there occurs in it a process of ordering of the magnetic moments of the erbium ions, accompanied by reorientation of the spins of the iron ions. For fuller understanding of the nature of this process, it is of interest to explain what influence an external magnetic field has on it.

In continuation of investigations in this direction begun by us,[3-5] we have made measurements of the NMR frequency in $ErFeO_3$ over quite wide intervals of temperature and of magnetic field. The results of the measurements indicate that the spin-reorientation processes induced by an external magnetic field applied along the c axis of the crystal remain continuous for temperatures $T \geq T_{cr} = 2.8 \pm 0.1$ K. For $T < T_{cr}$, phase transitions of the first order occur, and there appear two-phase states of the same type as the intermediate state in antiferromagnets.[6]

1. MEASUREMENT METHOD AND RESULTS

The NMR spectra of Fe^{57} in $ErFeO_3$ were taken over the temperature interval 1.65–4.2 K and in magnetic fields of magnitudes up to 6.5 kOe, by use of a spin-echo spectrometer with frequency sweep. The durations of the exciting pulses satisfied the condition for excitation of nuclei in domains ($\tau_2 = 2\tau_1$) and were $\tau_1 = 10$ μsec, $\tau_2 = 20$ μsec. The NMR linewidth was about 45 kHz. The $ErFeO_3$ single crystal used in the experiments was grown by the method of crucibleless zone melting, with optical heating.[7] The specimen had the form of a sphere of diameter ~5 mm. It was arranged in the cryostat in such a way that its crystallographic a axis, which had been previously determined by orientation of the weak ferromagnetic moment at nitrogen temperatures, was oriented perpendicular to the direction of the external magnetic field. By subsequent rotation of the specimen about the a axis, its c axis was oriented in the direction of the external magnetic field, which was monitored by measurements of the NMR frequencies.

The results of the measurements are conveniently exhibited in the form of graphs that determine the dependence of the NMR frequencies on the value of the external magnetic field. Two examples of such graphs are given in Fig. 1a and b. One of them relates to the case $T > T_{cr}$, the other to the case $T < T_{cr}$. In each of these cases, the NMR spectrum at $H_0 = 0$ consists of two resonance lines, corresponding to four iron ions equivalent in pairs in a magnetic structure of the type Γ_{12}, which is realized when $T < T_0 \approx 4$ K and $H_0 = 0$.[5] In weak magnetic fields, each of the resonance lines splits into two lines of about the same intensity; this indicates formation of a magnetic structure in which all the iron ions are nonequivalent. We believe that this magnetic structure is of the type Γ_{124}, in which modes of the three representations Γ_1,

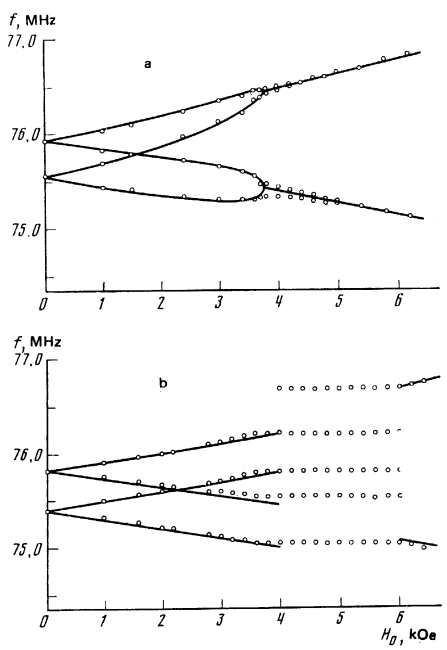

FIG. 1. Variation of NMR frequencies of Fe^{57} in $ErFeO_3$ with value of the external magnetic field H_0, at temperatures: a) 3.2 K; b) 1.65 K. Points, experiment; solid lines, calculation.

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Γ_2, and Γ_4 are present, although theoretically a small admixture of modes of the representation Γ_3 is allowed. In strong magnetic fields (of the order of 6 kOe and higher), the NMR spectra again consist of two resonance lines of about the same intensity; this indicates formation of a magnetic structure in which the iron ions are equivalent in pairs. This is probably a magnetic structure of the type Γ_{24}, in which the spins of the iron ions are ordered antiferromagnetically along the c axis (according to the mode $G_z \in \Gamma_2$), while the magnetic moments of the erbium ions are ordered ferromagnetically along the same axis (according to the mode $F_{Rz} \in \Gamma_4$).

It is quite clear that the qualitative difference between the two graphs in Fig. 1 is explained by the fact that in one case (Fig. 1a) the spin-reorientation process occurs continuously, whereas in the other case (Fig. 1b) there is a phase transition of first order, during which, over a certain interval of external magnetic fields, two phases coexist, and each of them produces its lines in the NMR spectrum. It is noteworthy that within this interval, the resonance frequencies do not change. This means that the local magnetic fields on the nuclei of the iron ions, and consequently also the internal magnetic fields on the ions themselves, remain constant, as is characteristic of the intermediate state of antiferromagnets.[6] On change of the external magnetic field within this interval, the intensities of the NMR lines from the two phases are redistributed. Therefore in order to determine the boundaries of the region of coexistence of the phases, it was necessary to follow each of the resonance lines until it disappeared in noise. It was assumed that a line had disappeared if the signal/noise ratio was approximately unity.

The region of coexistence of phases is shown in Fig. 2. It was obtained from the results of measurements similar to those shown in Fig. 1b. The width of this region decreases with rise of temperature and disappears when $T = T_{cr}$. Measurements of it at temperatures close to the critical are impeded by the fact that the NMR frequencies from the two phases differ little. Therefore the value of the critical temperature was not determined very accurately (the error is of the order of 0.1 K).

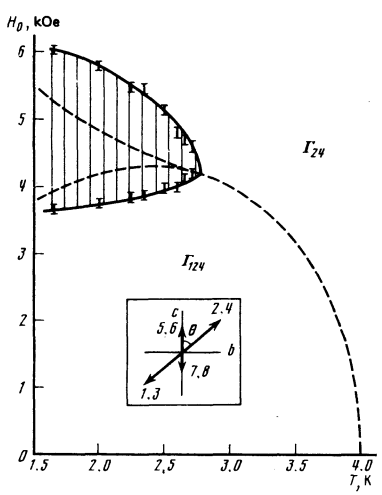

FIG. 2. Phase diagram of $ErFeO_3$. The region of coexistence of phases is shaded. The calculated phase diagram is shown by the dashed lines. The inset shows schematically the magnetic structure of the orthoferrite in the phase Γ_{124}.

Thus the results obtained enable us to suppose that an external magnetic field, applied along the c axis, produces a magnetostructural transformation of the type $\Gamma_{12} - \Gamma_{124} - \Gamma_{24}$, which, depending on the temperature, may occur as a phase transition of the second kind or as a phase transition of first order through an intermediate state.

2. DISCUSSION

The results obtained can be explained theoretically within the framework of the general approach[8] proposed for description of low-temperature spin-reorientation processes in rare-earth orthoferrites, by starting with a simple model that allows for interaction of the fundamental modes in the magnetic structure Γ_{124}: G_y, G_z, C_{Rz}, and F_{Rz}. Some other modes, for example C_{Ry} and G_x, could be included among the fundamental modes. This would lead to a more accurate but considerably more complicated and less comprehensible model.

The magnetic structure corresponding to the simple model is shown in the inset of Fig. 2. The original expression for the free energy of the system in this model has the following form:

$$F = U - TS, \tag{1}$$

where U is the internal energy of the system,

$$U = {}^1/_2 N[a_{11}G_y^2 + a_{22}C_{Rz}^2 + 2a_{12}G_yC_{Rz}] + {}^1/_2 N[b_{11}G_z^2 + c_{22}F_{Rz}^2] - 4Ng_{zz}\mu_B H_0 F_{Rz}, \tag{2}$$

and S is the entropy of the system of rare-earth ions, which are treated as particles with effective spin $s = \frac{1}{2}$ and with anisotropic (tensor) g factors:

$$-TS = 2kTN[({}^1/_2+s_1)\ln({}^1/_2+s_1) + ({}^1/_2-s_1)\ln({}^1/_2-s_1)] + 2kTN[({}^1/_2+s_2)\ln({}^1/_2+s_2) + ({}^1/_2-s_2)\ln({}^1/_2-s_2)]. \tag{3}$$

Here s_1 and s_2 are the values of the vectors that are obtained by thermodynamic averaging of the effective-spin operators of nonequivalent erbium ions, and N is the number of elementary cells in the crystal.

It can be shown that by minimization of the free energy of the system with respect to the orientation of the vector **G**, one obtains exactly the same expression as in the theory of metamagnetic phase transitions,[9] namely:

$$f = F/8kT_0N = (-l^2 + \tau_f m^2 - hm) + {}^1/_4\tau[({}^1/_2+m+l)\ln({}^1/_2+m+l) + ({}^1/_2-m-l)\ln({}^1/_2-m-l)] + {}^1/_4\tau[({}^1/_2+m-l)\ln({}^1/_2+m-l) + ({}^1/_2-m+l)\ln({}^1/_2-m+l)], \tag{4}$$

where $l = C_{Rz}$, $m = F_{Rz}$, $\tau = T/T_0$ is a dimensionless temperature parameter, $h = g_{zz}\mu_B H_0/2kT_0$ is a dimensionless field parameter; T_0 has the meaning of the temperature at which spontaneous spin reorientation begins, and τ_f is a dimensionless parameter proportional to c_{22}.

Thus the model under consideration reduces to the well studied model of metamagnets.[9] This circumstance allows us to omit the details of our numerical analysis of the model. We present only certain formulas that

were used in the numerical processing of the experimental results:

$$2\tau_f m+\frac{1}{2}\tau\ln\left(\frac{1+2m}{1-2m}\right)=h \tag{5}$$

the equation that determines the function $m(\tau,h)$ in the phase Γ_{24};

$$m=[{}^1/_4+l^2-l\operatorname{cth}(4l/\tau)]^{1/2}, \tag{6}$$

$$2\tau_f m(l)+\frac{1}{4}\tau\ln\left[\frac{({}^1/_2+m(l))^2-l^2}{({}^1/_2-m(l))^2-l^2}\right]=h \tag{7}$$

the equations that determine the functions $l(\tau,h)$ and $m(\tau,h)$ in the phase Γ_{124}.

The formulas necessary for calculation of the NMR frequencies were obtained on the basis of symmetry considerations, as was done earlier[5] for the case $H_0=0$:

$$\begin{aligned}
f_1&=f_0+\frac{1}{2}A\sin 2\theta-B\sin^2\theta-(\beta\sin\theta+\alpha\cos\theta)F_{Rz}+\frac{\gamma_n}{2\pi}H_0\cos\theta,\\
f_2&=f_0-\frac{1}{2}A\sin 2\theta-B\sin^2\theta-(\beta\sin\theta-\alpha\cos\theta)F_{Rz}-\frac{\gamma_n}{2\pi}H_0\cos\theta,\\
f_3&=f_0-\frac{1}{2}A\sin 2\theta-B\sin^2\theta+(\beta\sin\theta-\alpha\cos\theta)F_{Rz}+\frac{\gamma_n}{2\pi}H_0\cos\theta,\\
f_4&=f_0+\frac{1}{2}A\sin 2\theta-B\sin^2\theta+(\beta\sin\theta+\alpha\cos\theta)F_{Rz}-\frac{\gamma_n}{2\pi}H_0\cos\theta.
\end{aligned} \tag{8}$$

Here θ is the angle between the spins of the iron ions and the c axis [$\sin\theta\sim l$, as follows from the derivation of (4)]; $\gamma_n/2\pi$ is the gyromagnetic ratio for the Fe^{57} nucleus; f_0, A, and B are constants whose values were determined in Ref. 5; and α and β are constants that describe the contribution of the magnetized system of erbium ions to the NMR frequencies.

The value of the parameter τ_f was determined so as to obtain agreement between the experimental and calculated values of the critical temperature. We assumed that $\tau_f=-0.05$. Then according to Ref. 9

$$\tau_{cr}=4/3-1/3\tau_c=4/3-2/3(1-\tau_f)\approx 0.7,\quad T_{cr}\approx 2.8\ \text{K}$$

and a phase diagram of the type shown in Fig. 1a of Ref. 9 is obtained. It is shown in Fig. 2 by the dashed lines. In plotting it, we supposed that $g_{zz}=11.5$ in erbium orthoferrite.[10]

The calculated variations of the NMR frequencies with the value of the external magnetic field at temperatures 3.2 and 1.65 K are shown in Figs. 1a and b by the solid lines (in the calculation it was assumed that the values of the adjustable parameters α and β and the coefficient k in the relation $\sin\theta=kl$ were $\alpha=65$ kHz, $\beta=630$ kHz, $k=1.51$; with this choice of the value of k, the limiting angle θ for $T\to 0$ is approximately 49° [5]). There is good agreement on the whole between the experimental and calculated values of the NMR frequencies; there are small deviations, in particular, in the vicinity of the phase-transition point (Fig. 1a).

It should be mentioned that the effect of an external magnetic field on the low-temperature spin reorientation in $ErFeO_3$ was treated theoretically for the case of weak magnetic fields in Ref. 11 and in the general case in Ref. 12. The theory proposed in the latter paper can in principle be used to explain our experimental results. But application of this theory is impeded by the absence of specific solutions of the quite complicated system of equations.

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[1]G. Gorodetsky, R. M. Hornreich, I. Yaeger, H. Pinto, G. Shachar, and H. Shaked, Phys. Rev. **B8**, 3398 (1973).
[2]F. Vigneron, J. Phys. (Paris) **37**, 103 (1976).
[3]V. M. Khmara, N. M. Kovtun, and G. A. Troitskii, Solid State Commun. **15**, 1769 (1974).
[4]V. A. Klochan, N. M. Kovtun, and V. M. Khmara, Zh. Eksp. Teor. Fiz. **68**, 721 (1975) [Sov. Phys. JETP **41**, 357 (1975)].
[5]V. A. Klochan, N. M. Kovtun, and V. M. Khmara, Fiz. Nizk. Temp. **1**, 1287 (1975) [Sov. J. Low Temp. Phys. **1**, 616 (1975)].
[6]V. G. Bar'yakhtar, A. E. Borovik, and V. A. Popov, Pis'ma Zh. Eksp. Teor. Fiz. **9**, 634 (1969) [JETP Lett. **9**, 391 (1969)].
[7]A. V. Antonov, A. M. Bal'bashov, and A. Ya. Chervonenkis, Fiz. Tverd. Tela (Leningrad) **12**, 1724 (1970) [Sov. Phys. Solid State **12**, 1363 (1970)].
[8]V. A. Klochan, Author's abstract, candidate's dissertation, Donets, 1978.
[9]V. G. Bar'yakhtar, I. M. Vitebskiĭ, and D. A. Yablonskiĭ, Fiz. Tverd. Tela (Leningrad) **19**, 2135 (1977) [Sov. Phys. Solid State **19**, 1249 (1977)].
[10]D. L. Wood, L. M. Holmes, and J. P. Remeika, Phys. Rev. **185**, 689 (1969).
[11]I. M. Vitebskiĭ and D. A. Yablonskiĭ, Fiz. Tver. Tela (Leningrad) **20**, 2300 (1978) [Sov. Phys. Solid State **20**, 1327 (1978)].
[12]A. M. Kadomtseva, I. B. Krynetskiĭ, and V. M. Matveev, Zh. Eksp. Teor. Fiz. **79**, 1451 (1980) [Sov. Phys. JETP **52**, 732 (1980)].

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